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Electronic Supplementary Information

Nanoporous Amide Networks Based on Tetraphenyladamantane for Selective CO_2 Capture

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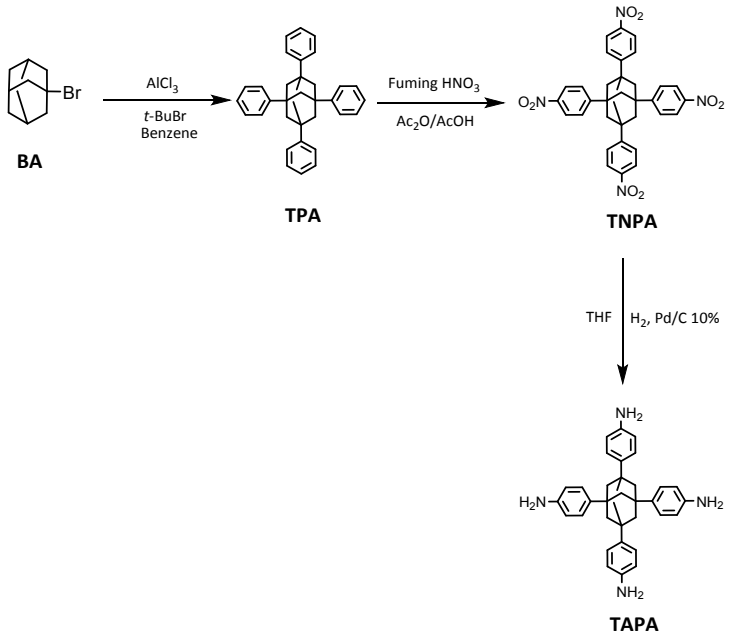
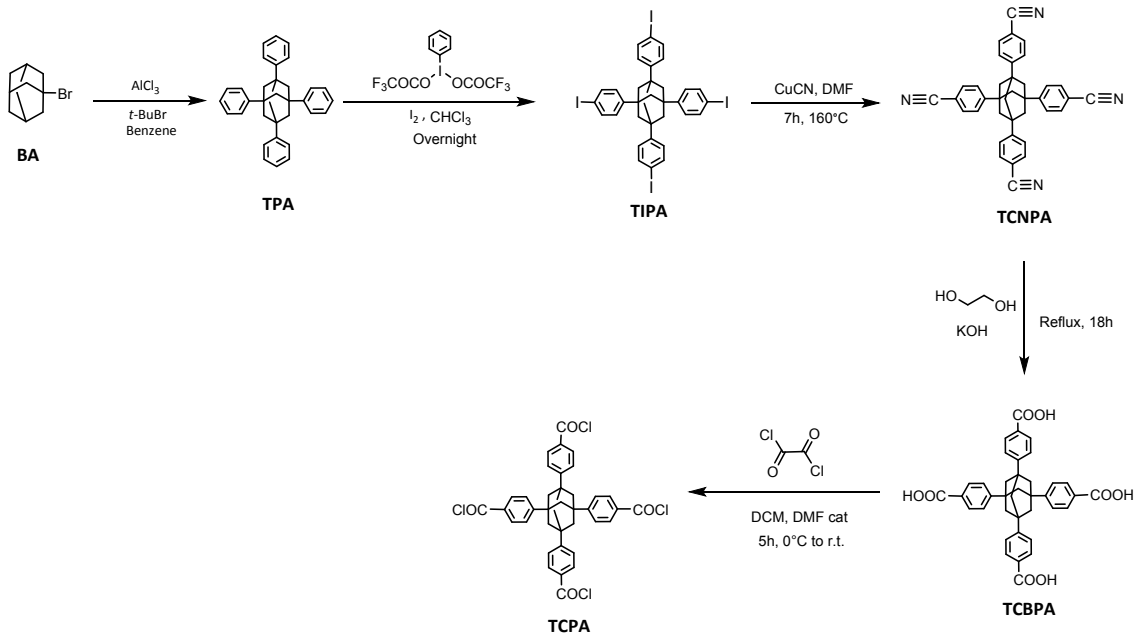


Scheme S1. Schematic for the synthesis of TAPA monomer.



Scheme S2. Schematic for the synthesis of TCPA monomer.

Synthesis of 1,3,5,7-tetraphenyladamantane (TPA)[S1]

1-Bromoadamantane (BA) (15g) and anhydrous $AlCl_3$ (0.75g) were charged in a dry three-neck round bottom flask (1000mL) equipped with a condenser, nitrogen inlet, dropping funnel and a magnetic bar. The flask was sealed properly to prevent reaction of $AlCl_3$ with moisture and kept in an ice bath. The top of condenser was linked to a hose whose end was immersed in a 50% KOH solution for removing HBr gas produced during the reaction. A solution of 2-bromo-2-methylpropane (*t*-BuBr) (15.6mL) in 150mL of benzene was taken in the dropping funnel and added drop-wise into contents of the flask with continuous stirring. The slow addition is essential because of release of significant amount of HBr gas. More ice has been added to the bath as required in order to avoid boiling of the solvent. After complete addition of *t*-BuBr solution for about 2h, the flask was kept in an oil bath and mixture was refluxed for 5h. A reasonable amount of white solid was formed during this time. The suspension was cooled to room temperature and then poured in 600mL of water containing 15mL of HCl (37%) with constant agitation. After 30min, the suspension was filtered and washed with 100mL of water, 200mL of acetone and thrice with 150mL of chloroform to afford TPA as a white solid. TPA was dried in vacuum oven at ambient temperature. Yield: 60%; Elemental analysis (CHN): 92.68 %C (91.09), 7.32 %H (7.05); FTIR (cm^{-1}): 3107 (=C-H), 2919, 2850(C-H), 1493 (C=C), 700 (Ar-H). Since TPA was insoluble in common organic solvents that's why NMR has not been recorded.

Synthesis of 1,3,5,7-tetrakis-(4-nitrophenyl)adamantane (TNPA)[S2]

Freshly synthesized fuming nitric acid (60mL) was cooled using an ice-salt bath (-18°C) and then (8.4g) of TPA was added to it in small portions with uninterrupted stirring for 1.5h. The solution became clear and stirred for additional 30 min at temperature below -10°C. Subsequently, 75mL of acetic anhydride: glacial acetic acid (1:2) solution was slowly added and stirring was continued for 15 min. The reaction mixture was poured into a beaker containing 100mL of glacial acetic acid forming white precipitates that were filtered off. Afterwards, the precipitates were washed again with glacial acetic acid and dried under vacuum at ambient temperature. Recrystallization from DMSO afforded TNPA as yellow needle-shaped crystals. Yield: 55%; m.p. >300°C; Elemental analysis (CHN): 65.80 %C (64.57), 4.55 %H (4.89), 9.03 %N (10.15); FTIR (cm^{-1}): 3110 (=C-H), 2924, 2850 (C-H), 1591, 1512 (C=C), 1341 (N=O), 856 (Ar-H); ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 8.23 (d, *J* = 8.4 Hz, 8H), 7.94 (d, *J* = 8.6 Hz, 8H), 2.25 (s, 12H).

Synthesis of 1,3,5,7-tetrakis-(4-aminophenyl)adamantane (TAPA)[S2]

TNPA (1g) was dissolved in 250mL of anhydrous THF at room temperature. Then to this solution, 0.1g of 10 wt.% Pd/C was added without stirring under N_2 atmosphere. The suspension was deaerated by 3 hydrogen-vacuum cycles and stirred for 3h at room temperature. The mixture was filtered through a double layered filter paper. The resulting solution was precipitated in 400mL of *i*-pentane and then filtered. The precipitates were dried under vacuum at room temperature yielding TAPA as a yellow fine powder. Yield: ~100%; m.p. >300°C; Elemental analysis (CHN): 81.56 %C (81.24), 7.25 %H (7.23), 11.19 %N (11.07); FTIR (cm^{-1}): 3433, 3357 (N-H), 3010 (=C-H), 2922, 2848 (C-H), 1619 (N-H), 1511 (C=C),

1117(C-N), 884 (Ar-H); ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.14 (d, *J* = 8.0 Hz, 8H), 6.52 (d, *J* = 7.9 Hz, 8H), 4.82 (s, 8H), 1.83 (s, 12H).

Synthesis of 1,3,5,7-tetrakis-(4-iodophenyl)adamantane (TIPA).[S3,S4]

To a suspension of TPA (4g) in $CHCl_3$ (100mL), I_2 (2g) was added and stirred until I_2 was fully dissolved. Afterwards, [bis-(trifluoroacetoxy)iodo]benzene (2g) was added and stirred for 2h. Then to this suspension, I_2 (2g) was added again together with [bis-(trifluoroacetoxy)iodo]benzene (2g) and stirred for 2h. Subsequently, more I_2 was added (5.2g) to the suspension followed by [bis-(trifluoroacetoxy)iodo]benzene (7.8g) and left for stirring overnight. The suspension was filtered and the solid was washed quickly with chloroform. The solid obtained was dissolved in 400mL of chloroform and washed with a 100mL solution of 5% sodium metabisulfite in water. The organic phase was then washed with 100mL of water and 100mL of brine followed by drying of water over Na_2SO_4 and later removal of the chloroform at reduced pressure. The yellow product was isolated and washed with 20mL of methanol thrice. Yield: 60%; Elemental analysis (CHN): 43.25 %C (43.29), 2.99 %H (3.01); FTIR (cm^{-1}): 3075(=C-H), 2928, 2851(C-H), 1488(H-C-H), 1392(-C-H), 1012(=C-H), 822(Ar-H), 778(Ar-H), 663(C-I); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.70 (d, *J* = 8.1 Hz, 8H), 7.21 (d, *J* = 8.1 Hz, 8H), 2.09 (s, 12H).

Synthesis of 1,3,5,7-tetrakis-(4-cyanophenyl)adamantane (TCNPA).[S5]

In 500mL round bottom flask, (14.3g) of TIPA and (6.45g) of copper cyanide in 120 mL of anhydrous DMF were heated at 160°C with continuous stirring for 7h. The resulted copper iodide precipitates were removed by filtration while hot and poured in to a solution of 15g of KCN in 300mL of water. The solid formed was isolated by filtration and dissolved in 50mL of hot DMF and the solution was immediately poured into 300mL of 10% HCl. The resulting solid was filtered and washed with water. Yield: 65%; Elemental analysis (CHN): 84.18 %C (83.41), 6.00 %H (5.92), 9.82 %N (10.08); FTIR (cm^{-1}): 3047(=C-H), 2924, 2848(C-H), 2226(C≡N), 1650 (C=C), 1498 (H-C-H), 1306 (ov. Ar-H), 835, 565(Ar-H); ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 2.15 (s, 12H); 7.83 (s, 16H).

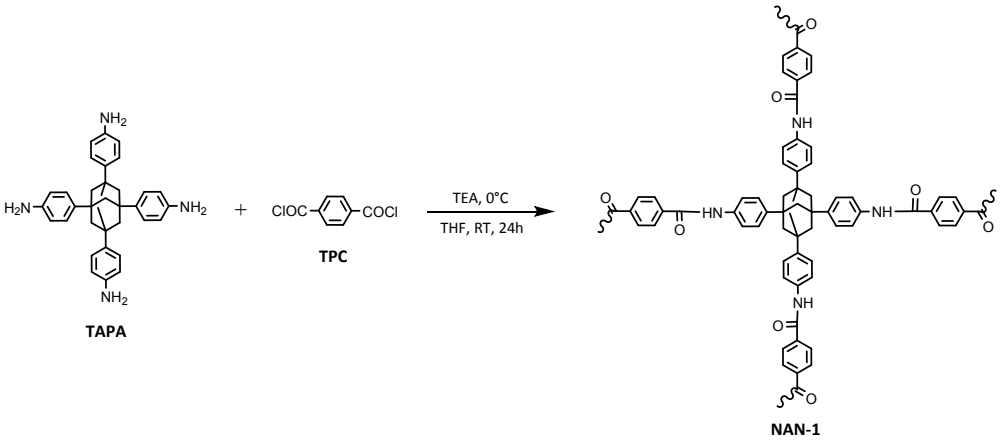
Synthesis of 1,3,5,7-tetrakis-(4-carboxyphenyl)adamantane (TCBPA).[S6]

A mixture of TCNPA (7.3g), potassium hydroxide (13.62g), and ethylene glycol (100mL) was heated under reflux for overnight; afterwards 250mL of water was added and the aqueous phase was washed thrice with 50mL of dichloromethane. To the aqueous phase, 500mL of 3M HCl was added with the immediate precipitation of solid which was washed with water and dried under reduced pressure. The solid was purified by repeatedly adding heptane followed by evaporation until yielded pure product. Yield: 55%; Elemental analysis (CHN): 74.01 %C (73.42), 5.23 %H (5.21); FTIR (cm^{-1}): 3076 (*b*, COOH), 2926, 2849(C-H), 2661, 2538(O-H), 1675(C=O), 1604, 1413(Ar-H), 1276(C-O), 842, 755, 539 (Ar-H); ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 2.18 (br s, 12H), 7.74 (d, *J* = 8.1 Hz, 8H), 7.93 (d, *J* = 8.1 Hz, 8H), 12.93 (br s, 4H).

Synthesis of 1,3,5,7-tetrakis(4-(chlorocarbonyl)phenyl)adamantane (TCPA)[S7]

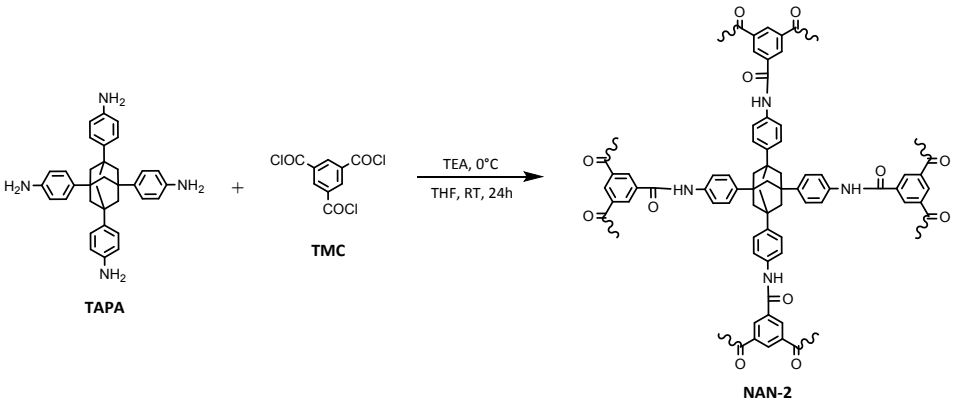
Oxalyl chloride (7.2mL) was added to TCBPA (1.25g) in anhydrous dichloromethane (15mL) at 0°C and then a catalytic amount of anhydrous DMF (0.1mL) was added drop-wise via a syringe for about 4h in an ice bath. Then the mixture was stirred for 1h at room temperature, and the excess of oxalyl chloride and solvent was removed under reduced pressure. Due to the reactive nature and air sensitivity of the product, it was directly used in-situ for the synthesis of NAN-3. Yield: ~100%.

Synthesis of porous amide network from TAPA and TPC (NAN-1)



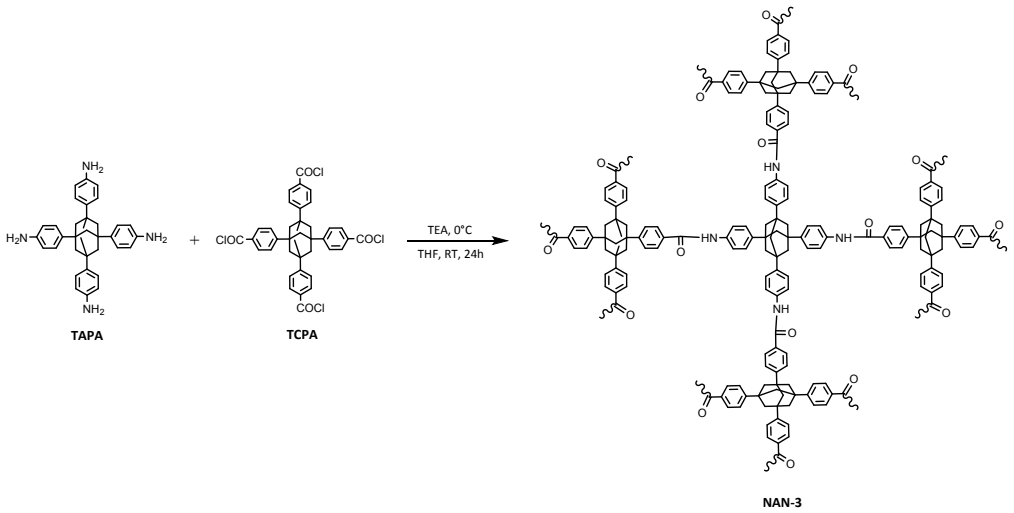
In a 250mL round bottom flask, TAPA (1g) was dissolved in 70mL of THF resulting in a bright mango colored solution. To this solution, 1.12mL of triethylamine (TEA) was added with continuous stirring. In another flask, a solution of TPC (0.8g) in 5mL of THF was prepared and added drop wise to the tetraamine solution with constant agitation under inert atmosphere. Owing to the exothermicity of polymerization reaction, the contents of flask were cooled at 0°C for 1 h. The reaction mixture became highly viscous and dense light lemon yellow precipitates were formed immediately after adding TPC. Further agitation was continued at room temperature for 24h to complete the polycondensation reaction. The precipitates were collected by filtration and washed several times with THF, water, and acetone to remove hydrochloride salt and organic oligomeric impurities. The resultant powder was then immersed in acetone for two days during which time the acetone was decanted and freshly replenished three times and dried under vacuum for 24h to afford a light lemon yellow colored powder. Yield: 70%; Elemental analysis (CHN): 77.33 %C (76.57), 4.72 %H (5.88), 5.47 %N (6.01); FTIR (cm^{-1}): 3344 (N-H), 2928, 2852 (C-H), 1653 (C=O), 1599, 1514, 1404 (C=C); CP/MAS ^{13}C NMR δ (ppm): 165.8 (Amide C=O), 125.2-145.5 (aromatic carbons of phenyl moiety), 38.5, 45.9 (secondary and tertiary carbon atoms of adamantane).

Synthesis of porous amide network from TAPA and TMC (NAN-2)



TAPA (1g) was dissolved in 70mL of THF in a 250mL round bottom flask equipped with a magnetic bar. Upon dissolution, TAPA gave a bright mango colored solution. Subsequently, triethylamine (TEA) (0.745mL) was added to this solution with uninterrupted agitation. In a separate flask, a solution of TMC (0.708g) in 5mL of THF was made and introduced drop wise to tetraamine solution with continuous stirring under anhydrous conditions. The polyamidation reaction was highly exothermic and carried out at 0°C for 1h in order to avoid any side reactions. As the reaction proceeds, dull orangish yellow precipitates were formed and solution became highly viscous. In order to ensure completion of condensation reaction, further 24h has been given. The solution was filtered and precipitates were washed many times with THF, water, and acetone so as to get rid of organic oligomeric impurities and the hydrochloride salt. The precipitates were dipped in acetone for two days and the fresh solvent was refilled at regular intervals. The precipitates were dried under reduced pressure for 24h yielding dull orangish yellow powder. Yield: 55%; Elemental analysis (CHN): 74.19 %C (73.25), 3.91 %H (4.63), 4.94 %N (5.87); FTIR (cm^{-1}): 3342 (N-H), 2926, 2852 (C-H), 1653 (C=O), 1599, 1514, 1401 (C=C); CP/MAS ^{13}C NMR δ (ppm): 166.1 (Amide C=O), 125-145.7 (aromatic carbons of phenyl moiety), 38.4, 45.5 (secondary and tertiary carbon atoms of adamantane).

Synthesis of porous amide network from TAPA and TCPA (NAN-3)



In a 250mL round bottom flask, TAPA (1g) was dissolved in 70mL of THF resulting in a bright mango colored solution. To this solution, 0.56mL of triethylamine (TEA) was added with continuous stirring. In another flask, a solution of TCPA (1.381g) in THF was prepared and added drop wise to the tetraamine solution with constant agitation under inert atmosphere. Owing to the exothermicity of polymerization reaction, the contents of flask were cooled at 0°C for 1 h. The reaction mixture became highly viscous and yellowish brown precipitates were formed immediately after adding TCPA. Further agitation was continued at room temperature for 24h to complete the polycondensation reaction. The precipitates were collected by filtration and washed several times with THF, water, and acetone to remove hydrochloride salt and organic oligomeric impurities. The resultant powder was then immersed in acetone for two days during which time the acetone was decanted and freshly replenished three times and dried under vacuum for 24h to afford a light brown colored powder. Yield: 65%; Elemental analysis (CHN): 83.01 %C (81.53), 5.39 %H (6.87), 2.08 %N (3.19); FTIR (cm^{-1}): 3356 (N-H), 2927, 2852(C-H), 1688 (C=O), 1600, 1513, 1403 (C=C); CP/MAS ^{13}C NMR δ (ppm): 160.9 (Amide C=O), 125.2-153.7 (aromatic carbons of phenyl moiety), 38.9, 47.5 (secondary and tertiary carbon atoms of adamantane).

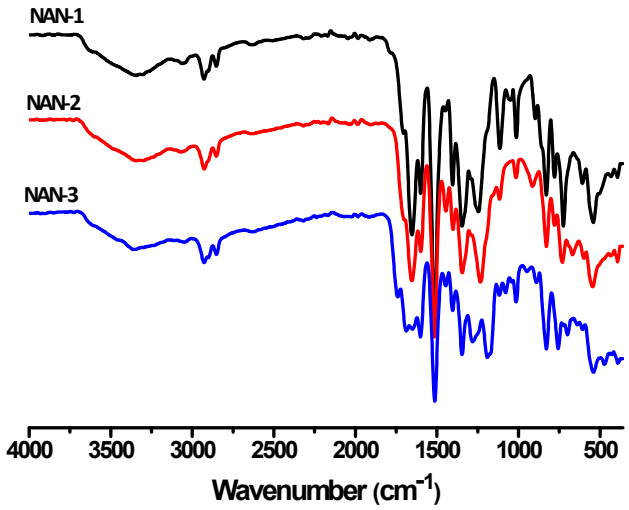


Fig. S1 FTIR spectra of NANs

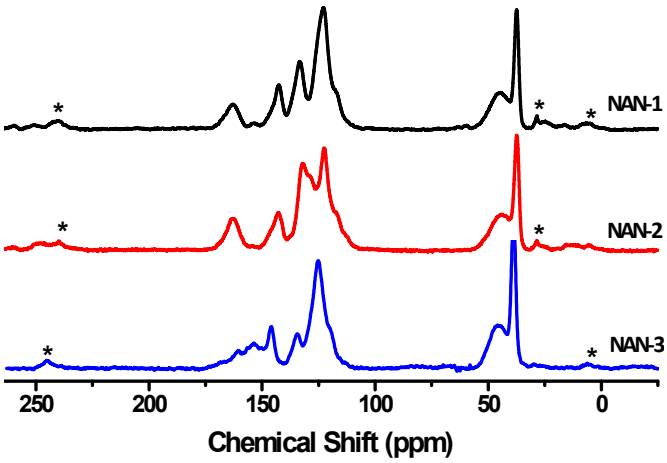


Fig. S2 Solid state CP/MAS ^{13}C NMR spectra of NANs. Asterisks (*) indicate spinning side bands.

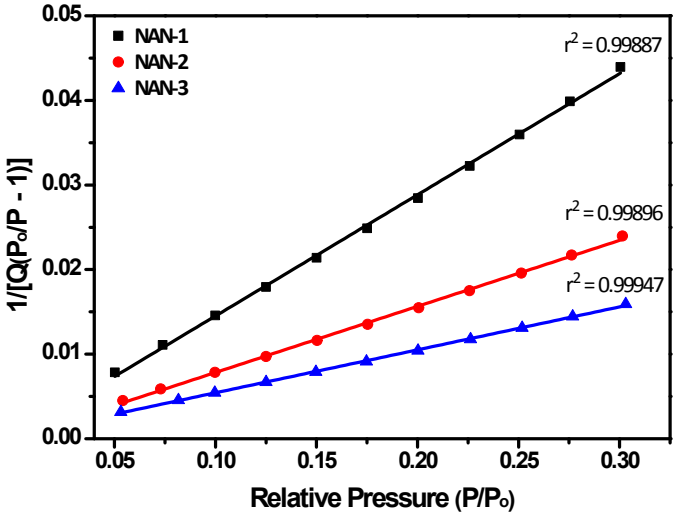


Fig. S3 BET linear plots (P/P_o = 0.05-0.3) of NANs from N_2 isotherms at 77K.

Table S1. Cartesian coordinates of CO_2 and N_2

C	-0.807799	0.473538	0.000000	N	-0.389338	0.988539	0.000000
O	0.356844	0.473538	0.000000	N	-1.490628	0.988539	0.000000
O	-1.972443	0.473538	0.000000				

Table S2. Cartesian coordinates of NAN-1, NAN-1/CO_2 and NAN-1/N_2 complexes

NAN-1				**NAN-1/CO_2 complex**				**NAN-1/N_2 complex**			
C	1.383235	1.606440	-0.211762	C	1.046511	1.159694	-0.291954	C	1.407907	-1.480712	-0.142770
C	0.688483	0.400266	-0.102150	C	0.310048	-0.013448	-0.116912	C	0.727297	-0.267335	-0.261578
C	-0.688511	0.400281	0.102206	C	-1.063672	0.048046	0.098987	C	-0.643136	-0.253538	-0.504562
C	-1.383243	1.606470	0.211772	C	-1.712177	1.283455	0.154685	C	-1.342628	-1.452754	-0.648951
C	-0.683957	2.812423	0.115546	C	-0.969798	2.456647	-0.003766	C	-0.656923	-2.665784	-0.554616
C	0.683967	2.812408	-0.115579	C	0.394718	2.394717	-0.245721	C	0.702796	-2.679760	-0.278813
H	1.206090	-0.549257	-0.205817	H	0.793319	-0.984364	-0.178405	H	1.247795	0.676731	-0.126867
H	-1.206137	-0.549229	0.205897	H	-1.614891	-0.875348	0.253156	H	-1.157795	0.698672	-0.596265
H	-1.230425	3.743108	0.223614	H	-1.480619	3.411036	0.064397	H	-1.206656	-3.591337	-0.688297
H	1.230450	3.743079	-0.223687	H	0.974367	3.298198	-0.400617	H	1.238424	-3.615816	-0.163153
C	-2.865068	1.676283	0.465713	C	-3.189113	1.422043	0.410367	C	-2.823887	-1.498676	-0.905640
O	-3.349680	2.581038	1.128270	O	-3.635546	2.377438	1.027021	O	-3.313118	-2.328365	-1.656986
N	-3.589908	0.667479	-0.109373	N	-3.954458	0.414239	-0.111116	N	-3.539297	-0.558326	-0.214375
H	-3.086365	0.064872	-0.742412	H	-3.476348	-0.240447	-0.711299	H	-3.026044	-0.039978	0.483495
C	2.865056	1.676222	-0.465739	C	2.523892	1.158108	-0.563272	C	2.878451	-1.569822	0.165749
O	3.349666	2.580955	-1.128327	O	3.039811	2.013399	-1.269013	O	3.329050	-2.497979	0.819994
N	3.589907	0.667465	0.109413	N	3.219131	0.144775	0.039635	N	3.633726	-0.551597	-0.350032
H	3.086378	0.064902	0.742505	H	2.727033	-0.367249	0.756271	H	3.160711	0.075777	-0.982603
C	4.979617	0.431501	0.041294	C	4.611579	-0.085485	-0.019880	C	5.022822	-0.335338	-0.225013
C	5.850204	1.152312	-0.774472	C	5.401193	0.319563	-1.093655	C	5.857097	-1.100002	0.588858
C	5.494757	-0.599881	0.834813	C	5.209654	-0.773476	1.039910	C	5.576531	0.720040	-0.958907
C	7.208172	0.832102	-0.783969	C	6.769267	0.048835	-1.085763	C	7.218325	-0.800852	0.653248
H	5.472231	1.958024	-1.387839	H	4.960002	0.859092	-1.920796	H	5.449009	-1.923432	1.157790
C	6.847314	-0.899814	0.809635	C	6.569534	-1.042071	1.023224	C	6.931727	0.998365	-0.879788
H	4.831945	-1.173098	1.479381	H	4.609684	-1.089098	1.890013	H	4.942286	1.328688	-1.599799
C	7.744933	-0.191303	-0.001696	C	7.390086	-0.632549	-0.037568	C	7.793836	0.243810	-0.071329
H	7.850458	1.417582	-1.431646	H	7.348547	0.392796	-1.934511	H	7.831575	-1.421219	1.296582
H	7.204840	-1.707042	1.442036	H	6.997046	-1.574711	1.867487	H	7.320082	1.824827	-1.467682
C	-4.979617	0.431508	-0.041256	C	-5.353207	0.241358	-0.037353	C	-4.932178	-0.331812	-0.223018
C	-5.850227	1.152376	0.774435	C	-6.196376	1.048332	0.724715	C	-5.812213	-0.950774	-1.109288
C	-5.494732	-0.599938	-0.834708	C	-5.908009	-0.814239	-0.769953	C	-5.440308	0.580903	0.708359
C	-7.208194	0.832158	0.783925	C	-7.567491	0.790066	0.739942	C	-7.173331	-0.650006	-1.050439
H	-5.472275	1.958142	1.387744	H	-5.787058	1.872502	1.291710	H	-5.439304	-1.665117	-1.829732
C	-6.847286	-0.899885	-0.809530	C	-7.272745	-1.051761	-0.739916	C	-6.796243	0.864108	0.748524
H	-4.831904	-1.173194	-1.479224	H	-5.266871	-1.455292	-1.371077	H	-4.769284	1.071994	1.409671
C	-7.744927	-0.191323	0.001733	C	-8.143955	-0.254330	0.015836	C	-7.703604	0.255704	-0.130655
H	-7.850499	1.417687	1.431539	H	-8.187335	1.442544	1.343934	H	-7.823589	-1.154047	-1.756178
H	-7.204795	-1.707153	-1.441889	H	-7.661417	-1.880267	-1.324600	H	-7.148992	1.576890	1.488094
C	-9.228378	-0.552314	-0.005206	C	-9.642360	-0.547057	0.012529	C	-9.190369	0.593375	-0.048451
C	-9.418317	-2.029045	0.424473	C	-9.905432	-1.981663	0.536224	C	-9.404994	2.110620	-0.281650
C	-9.808940	-0.377201	-1.431415	C	-10.198236	-0.441198	-1.430324	C	-9.739862	0.229802	1.354447
C	-10.058998	0.327791	0.953005	C	-10.442147	0.431895	0.898201	C	-10.031528	-0.167888	-1.095285
H	-8.843586	-2.688947	-0.236473	H	-9.354265	-2.709527	-0.071369	H	-8.823628	2.687965	0.447412
H	-9.015659	-2.163997	1.436571	H	-9.520904	-2.066972	1.560693	H	-9.024651	2.379394	-1.275588
C	-10.901910	-2.426335	0.380991	C	-11.405315	-2.313081	0.497863	C	-10.891525	2.479645	-0.159646
H	-9.244788	-0.991273	-2.143698	H	-9.655263	-1.126288	-2.092477	H	-9.167506	0.754850	2.128780
H	-9.684728	0.667313	-1.744608	H	-10.022384	0.573418	-1.810040	H	-9.598688	-0.844609	1.528937
C	-11.292041	-0.776054	-1.472480	C	-11.697635	-0.774275	-1.466396	C	-11.226135	0.601153	1.474398
H	-9.680025	0.223526	1.977984	H	-10.080775	0.378964	1.933402	H	-9.675098	0.071328	-2.105685
H	-9.956079	1.384103	0.672882	H	-10.286977	1.461427	0.550522	H	-9.911839	-1.249990	-0.954523
C	-11.544437	-0.065320	0.916206	C	-11.943745	0.105157	0.865727	C	-11.519996	0.197975	-0.980274
H	-11.001413	-3.475681	0.682779	H	-11.556718	-3.334322	0.867025	H	-11.008213	3.557650	-0.322846

C	-11.437384	-2.246709	-1.048874	C	-11.915770	-2.205174	-0.948293	C	-11.395766	2.111878	1.245421
C	-11.699116	-1.532858	1.342811	C	-12.171175	-1.321973	1.386558	C	-11.698899	1.705975	-1.212577
H	-11.670197	-0.647420	-2.493519	H	-12.057596	-0.697296	-2.499139	H	-11.581691	0.337997	2.477664
C	-12.088832	0.115740	-0.508761	C	-12.463135	0.215297	-0.575718	C	-12.033370	-0.170627	0.419915
H	-12.099321	0.579817	1.607375	H	-12.475901	0.819621	1.504618	H	-12.082281	-0.360713	-1.737715
H	-12.491151	-2.549376	-1.096384	H	-12.981866	-2.461966	-0.990687	H	-12.451601	2.392052	1.351121
H	-10.884059	-2.894006	-1.741684	H	-11.385407	-2.921888	-1.588762	H	-10.835239	2.672582	2.004869
H	-11.335811	-1.667199	2.369695	H	-11.826315	-1.403506	2.425272	H	-11.358254	1.975303	-2.220586
H	-12.758705	-1.818333	1.334065	H	-13.242681	-1.558882	1.381411	H	-12.761157	1.974044	-1.147356
H	-12.005956	1.166887	-0.813123	H	-12.328081	1.238883	-0.947842	H	-11.933443	-1.250960	0.585934
H	-13.153539	-0.148103	-0.541863	H	-13.538494	-0.001360	-0.606505	H	-13.099959	0.073050	0.506597
C	9.228382	-0.552302	0.005216	C	8.886640	-0.932049	-0.005168	C	9.282854	0.577642	-0.022438
C	9.418263	-2.029153	-0.424071	C	9.121347	-2.461623	0.078869	C	9.487929	2.033758	0.466934
C	9.809078	-0.376801	1.431325	C	9.532400	-0.266903	1.236940	C	9.900585	0.443768	-1.437727
C	10.058925	0.327526	-0.953316	C	9.624206	-0.409519	-1.256422	C	10.069708	-0.353243	0.924818
H	8.843577	-2.688860	0.237110	H	8.613270	-2.871392	0.960120	H	8.944517	2.728714	-0.184656
H	9.015514	-2.164380	-1.436096	H	8.672815	-2.943474	-0.799420	H	9.059421	2.139511	1.471909
C	10.901857	-2.426449	-0.380611	C	10.621947	-2.782217	0.157399	C	10.979463	2.403005	0.479344
H	9.244993	-0.990672	2.143832	H	9.035186	-0.615592	2.150076	H	9.368379	1.094845	-2.141801
H	9.684905	0.667800	1.744240	H	9.377327	0.818416	1.185361	H	9.765708	-0.585843	-1.793209
C	11.292179	-0.775656	1.472363	C	11.032404	-0.590235	1.313934	C	11.391530	0.814430	-1.422718
H	9.679864	0.222972	-1.978232	H	9.197636	-0.866339	-2.158904	H	9.663680	-0.279744	1.942100
H	9.956035	1.383919	-0.673484	H	9.487522	0.676009	-1.344162	H	9.955578	-1.396298	0.602360
C	11.544363	-0.065591	-0.916544	C	11.125978	-0.728736	-1.185339	C	11.562596	0.011867	0.944125
H	11.001319	-3.475880	-0.682116	H	10.753584	-3.868739	0.222506	H	11.089831	3.438492	0.822619
C	11.437465	-2.246430	1.049155	C	11.222939	-2.113082	1.404249	C	11.552217	2.265438	-0.940822
C	11.698986	-1.533250	-1.342753	C	11.325466	-2.249412	-1.099605	C	11.732245	1.459497	1.429152
H	11.670430	-0.646743	2.493332	H	11.456992	-0.112124	2.204481	H	11.796104	0.715849	-2.436977
C	12.088891	0.115860	0.508322	C	11.735554	-0.059579	0.055822	C	12.143863	-0.127640	-0.471027
H	12.099191	0.579347	-1.607944	H	11.613330	-0.343357	-2.088485	H	12.085524	-0.669045	1.625918
H	12.491233	-2.549097	1.096651	H	12.290598	-2.354350	1.482474	H	12.612424	2.548807	-0.947489
H	10.884196	-2.893528	1.742195	H	10.737442	-2.499892	2.309674	H	11.031120	2.948627	-1.624188
H	11.335586	-1.667873	-2.369567	H	10.915459	-2.734496	-1.994665	H	11.342401	1.563199	2.449862
H	12.758573	-1.818735	-1.334024	H	12.396037	-2.487774	-1.063717	H	12.796805	1.724227	1.460455
H	12.006054	1.167094	0.812399	H	11.620438	1.029890	-0.008576	H	12.050020	-1.165156	-0.816449
H	13.153598	-0.147985	0.541400	H	12.811521	-0.269136	0.106900	H	13.213869	0.116124	-0.464904
				C	5.197704	3.340787	0.169887	N	-0.593768	-1.706560	2.972532
				O	4.641444	3.024093	1.144604	N	-1.327104	-0.955131	2.638512
				O	5.778898	3.687113	-0.777411				

Table S3. Cartesian coordinates of NAN-2, NAN-2/CO_2 and NAN-2/N_2 complexes

NAN-2				**NAN-2/CO_2 complex**				**NAN-2/N_2 complex**			
C	0.367950	-1.741174	-0.182345	C	0.125795	-1.957288	-0.182156	C	-0.093703	-1.859196	-0.120869
C	0.653511	-0.387317	0.008532	C	-0.238752	-0.612215	-0.266606	C	-0.422969	-0.511962	-0.280363
C	-0.374506	0.518534	0.269327	C	0.734943	0.377576	-0.386796	C	0.575971	0.440168	-0.476378
C	-1.688003	0.058492	0.360928	C	2.078282	0.007066	-0.448564	C	1.907542	0.031174	-0.542380
C	-1.983735	-1.285905	0.141297	C	2.451524	-1.332613	-0.345538	C	2.246323	-1.309380	-0.361451
C	-0.951233	-2.182908	-0.133048	C	1.470355	-2.314843	-0.207179	C	1.241190	-2.252655	-0.145583
H	1.684766	-0.045990	-0.038787	H	-1.292895	-0.354052	-0.230366	H	-1.466830	-0.213434	-0.248307
H	-2.451787	0.778469	0.640457	H	2.804411	0.798241	-0.611492	H	2.651706	0.789612	-0.768002
H	-1.179087	-3.231101	-0.294069	H	1.759914	-3.357357	-0.130028	H	1.504196	-3.295865	-0.007265
C	-0.142210	1.987209	0.506065	C	0.423162	1.848963	-0.487101	C	0.294289	1.909465	-0.648853
O	-0.887536	2.629371	1.231358	O	1.240255	2.626077	-0.961098	O	1.066352	2.625973	-1.269701
N	0.932578	2.512552	-0.155480	N	-0.800378	2.219832	-0.007375	N	-0.853693	2.347548	-0.050742
H	1.374967	1.913512	-0.835917	H	-1.347161	1.505364	0.448787	H	-1.335887	1.684739	0.537701
C	-3.380296	-1.847340	0.232262	C	3.884698	-1.794367	-0.422214	C	3.665109	-1.816198	-0.424028
O	-3.564927	-3.006633	0.569892	O	4.159974	-2.901943	-0.858199	O	3.903530	-2.957663	-0.788102
N	-4.374059	-0.969922	-0.098302	N	4.803953	-0.892825	0.034784	N	4.614565	-0.913908	-0.035532
H	-4.080801	-0.075049	-0.459350	H	4.437713	-0.057619	0.465542	H	4.276954	-0.040102	0.338142
C	1.443021	-2.752063	-0.481678	C	-0.913632	-3.026923	0.009569	C	-1.148690	-2.897957	0.147087

O	1.254100	-3.655056	-1.280683	O	-0.724768	-3.973402	0.756612	O	-0.956542	-3.804668	0.941098
N	2.607249	-2.556971	0.211582	N	-2.066015	-2.816349	-0.700750	N	-2.310293	-2.712460	-0.554793
H	2.574565	-1.867765	0.947973	H	-2.039817	-2.069133	-1.378121	H	-2.280821	-2.019349	-1.287663
C	1.433827	3.832660	-0.114793	C	-1.401656	3.497396	-0.014702	C	-1.410602	3.645210	-0.051454
C	2.472827	4.151942	-0.989703	C	-2.686736	3.600371	0.520286	C	-2.566590	3.845111	0.704443
C	0.958747	4.814814	0.758753	C	-0.788341	4.643761	-0.527668	C	-0.876110	4.719488	-0.768149
C	3.030808	5.425806	-0.995461	C	-3.350018	4.822333	0.545015	C	-3.178622	5.092891	0.749612
H	2.855642	3.401050	-1.677476	H	-3.180060	2.716857	0.918886	H	-2.997742	3.019700	1.266552
C	1.532178	6.080781	0.735434	C	-1.471957	5.853697	-0.493964	C	-1.506138	5.957231	-0.708818
H	0.148900	4.588538	1.437844	H	0.207314	4.583299	-0.943583	H	0.021190	4.584144	-1.355265
C	2.575467	6.425962	-0.132168	C	-2.760872	5.983416	0.036912	C	-2.664194	6.184272	0.044381
H	3.835446	5.624188	-1.693917	H	-4.346441	4.850500	0.970590	H	-4.073349	5.198602	1.352087
H	1.139344	6.820714	1.426613	H	-0.966907	6.724855	-0.900905	H	-1.064362	6.771484	-1.275799
C	3.807686	-3.298124	0.144710	C	-3.314855	-3.455330	-0.567102	C	-3.534589	-3.403514	-0.434412
C	4.812744	-2.977417	1.057891	C	-4.354836	-3.013598	-1.388159	C	-4.561866	-3.049332	-1.309776
C	4.039758	-4.312545	-0.788336	C	-3.571278	-4.464087	0.366354	C	-3.776542	-4.382939	0.532761
C	6.027239	-3.654856	1.045095	C	-5.630854	-3.554788	-1.270708	C	-5.811090	-3.653879	-1.220314
H	4.650307	-2.191388	1.792163	H	-4.170734	-2.236624	-2.127038	H	-4.391177	-2.290196	-2.070099
C	5.261591	-4.975305	-0.782626	C	-4.855444	-4.985734	0.467714	C	-5.033835	-4.970999	0.605190
H	3.269655	-4.581128	-1.497681	H	-2.773536	-4.830051	0.997880	H	-2.988927	-4.678306	1.211760
C	6.284808	-4.674073	0.124363	C	-5.917915	-4.550437	-0.333431	C	-6.082484	-4.629428	-0.257195
H	6.774634	-3.369880	1.776343	H	-6.404995	-3.176678	-1.928275	H	-6.576607	-3.344484	-1.922397
H	5.408320	-5.759985	-1.519038	H	-5.022568	-5.762071	1.208375	H	-5.189705	-5.725907	1.370244
C	-5.771436	-1.169923	-0.076249	C	6.211468	-0.999073	0.050053	C	6.018045	-1.064480	-0.011707
C	-6.576520	-0.117819	-0.514906	C	6.927191	0.044057	0.639158	C	6.769363	0.006817	0.473451
C	-6.379805	-2.348385	0.365204	C	6.914099	-2.075231	-0.499588	C	6.682856	-2.213487	-0.449609
C	-7.962086	-0.235206	-0.515015	C	8.316958	0.019021	0.679102	C	8.157179	-0.063413	0.523596
H	-6.121517	0.808082	-0.859745	H	6.398130	0.890573	1.071218	H	6.270037	0.910555	0.815765
C	-7.766659	-2.442214	0.357289	C	8.303203	-2.077618	-0.449418	C	8.070917	-2.260315	-0.391039
H	-5.772368	-3.175724	0.703642	H	6.376573	-2.895592	-0.953787	H	6.117033	-3.054700	-0.824220
C	-8.595807	-1.401725	-0.078397	C	9.043967	-1.042852	0.134231	C	8.846667	-1.200082	0.092641
H	-8.543079	0.610212	-0.864875	H	8.825723	0.853680	1.147202	H	8.695324	0.795015	0.908608
H	-8.206787	-3.371601	0.706784	H	8.817658	-2.928068	-0.887265	H	8.555776	-3.168097	-0.738258
C	3.158844	7.836473	-0.106757	C	-3.454208	7.343537	0.040984	C	-3.301295	7.571197	0.072360
C	3.727289	8.149650	1.300613	C	-3.589110	7.872856	-1.409392	C	-3.700627	8.001929	-1.361695
C	2.053378	8.872870	-0.432174	C	-2.620190	8.361270	0.859879	C	-2.292083	8.605242	0.632788
C	4.299562	8.027361	-1.129033	C	-4.868923	7.290270	0.656225	C	-4.569018	7.625994	0.951284
H	2.943423	8.026395	2.057229	H	-2.601312	7.927250	-1.881830	H	-2.822888	7.977604	-2.018210
H	4.516264	7.424969	1.539721	H	-4.183780	7.162498	-1.998079	H	-4.420654	7.279581	-1.767340
C	4.279966	9.581862	1.361895	C	-4.243676	9.262566	-1.427361	C	-4.303053	9.415344	-1.361572
H	1.223030	8.769604	0.276317	H	-1.605333	8.428813	0.450520	H	-1.375397	8.597387	0.031362
H	1.646887	8.664421	-1.430190	H	-2.522977	7.999671	1.891641	H	-2.005918	8.313439	1.651448
C	2.608378	10.304104	-0.368552	C	-3.276466	9.750292	0.839123	C	-2.896518	10.017654	0.630525
H	5.107906	7.313133	-0.924117	H	-5.493456	6.582706	0.095088	H	-5.312960	6.909745	0.578370
H	3.930717	7.822127	-2.142582	H	-4.812640	6.927605	1.691010	H	-4.322359	7.335364	1.980876
C	4.858691	9.458000	-1.072026	C	-5.531181	8.677400	0.639722	C	-5.178516	9.037056	0.954586
H	4.667170	9.773866	2.369434	H	-4.317595	9.610698	-2.464317	H	-4.567914	9.692253	-2.388736
C	3.153921	10.578481	1.042329	C	-3.384108	10.243165	-0.613097	C	-3.270868	10.411012	-0.807697
C	5.410257	9.738778	0.333937	C	-5.646653	9.175397	-0.808887	C	-5.559764	9.436040	-0.479020
H	1.802427	11.011583	-0.596195	H	-2.660446	10.446679	1.420063	H	-2.157420	10.724537	1.025430
C	3.740148	10.460232	-1.394966	C	-4.680403	9.662537	1.455534	C	-4.154495	10.037658	1.511318
H	5.663864	9.553947	-1.809864	H	-6.530711	8.598651	1.083251	H	-6.073843	9.035376	1.587280
H	3.532641	11.606474	1.105645	H	-3.831125	11.245070	-0.638018	H	-3.682935	11.427923	-0.824274
H	2.348136	10.485118	1.781807	H	-2.383804	10.324808	-1.057545	H	-2.374828	10.415383	-1.441643
H	6.227701	9.043481	0.564110	H	-6.274108	8.490936	-1.394079	H	-6.310560	8.741250	-0.876745
H	5.825618	10.753428	0.379968	H	-6.132383	10.159153	-0.831355	H	-6.009703	10.436870	-0.484410
H	3.356620	10.283813	-2.408058	H	-4.613323	9.328504	2.498854	H	-3.894580	9.775450	2.544875
H	4.133763	11.484288	-1.371558	H	-5.153447	10.652689	1.462354	H	-4.586183	11.046297	1.532006
C	7.599826	-5.448443	0.081736	C	-7.308892	-5.152093	-0.154662	C	-7.442584	-5.307963	-0.116632
C	8.604203	-4.975384	1.154292	C	-8.345154	-4.554833	-1.130353	C	-8.465484	-4.812472	-1.160990
C	8.272608	-5.278863	-1.304046	C	-7.811750	-4.891095	1.287997	C	-8.028514	-5.026631	1.290321
C	7.332265	-6.956850	0.316828	C	-7.262473	-6.682758	-0.391038	C	-7.294238	-6.840821	-0.290050
H	8.825339	-3.909047	1.014237	H	-8.412851	-3.468762	-0.983895	H	-8.604855	-3.727901	-1.061827

H	8.164402	-5.089829	2.153701	H	-8.025170	-4.726557	-2.166581	H	-8.086743	-5.002553	-2.173857
C	9.911744	-5.779892	1.079895	C	-9.731571	-5.182543	-0.915062	C	-9.820629	-5.515879	-0.983705
H	8.473027	-4.213961	-1.479240	H	-7.851800	-3.808860	1.465189	H	-8.143360	-3.942992	1.422340
H	7.588449	-5.607336	-2.095319	H	-7.099774	-5.303768	2.012511	H	-7.328311	-5.367605	2.062091
C	9.576018	-6.088577	-1.383052	C	-9.194468	-5.523697	1.507834	C	-9.379912	-5.734456	1.472591
H	6.860501	-7.089953	1.298837	H	-6.912815	-6.879512	-1.412674	H	-6.885346	-7.052832	-1.286271
H	6.621940	-7.331857	-0.429358	H	-6.536129	-7.145463	0.287368	H	-6.574395	-7.232822	0.438009
C	8.636927	-7.764057	0.235952	C	-8.645893	-7.312766	-0.168332	C	-8.646651	-7.546290	-0.105287
H	10.597050	-5.415673	1.854289	H	-10.437759	-4.734926	-1.624186	H	-10.517951	-5.138574	-1.740901
C	10.551437	-5.594715	-0.304406	C	-10.200529	-4.910775	0.522361	C	-10.372693	-5.221094	0.419180
C	9.613154	-7.268601	1.313095	C	-9.652285	-6.698188	-1.152263	C	-9.640316	-7.031472	-1.157015
H	10.022491	-5.953443	-2.375225	H	-9.518587	-5.328085	2.536711	H	-9.763675	-5.521666	2.477281
C	9.268144	-7.577176	-1.153325	C	-9.106017	-7.040505	1.273145	C	-9.189835	-7.250428	1.302097
H	8.412981	-8.824709	0.399455	H	-8.578284	-8.394070	-0.335709	H	-8.506536	-8.626801	-0.226567
H	11.493934	-6.153875	-0.361604	H	-11.196937	-5.342177	0.681144	H	-11.348029	-5.706760	0.549779
H	10.791942	-4.536714	-0.470218	H	-10.284395	-3.829898	0.693637	H	-10.529113	-4.141861	0.543653
H	9.178793	-7.414235	2.310420	H	-9.342032	-6.902579	-2.184988	H	-9.269861	-7.254283	-2.165786
H	10.543463	-7.849513	1.277081	H	-10.641535	-7.152924	-1.015414	H	-10.606122	-7.540685	-1.046884
H	8.583996	-7.943774	-1.929440	H	-8.401157	-7.490454	1.984127	H	-8.493706	-7.629914	2.061186
H	10.189834	-8.167830	-1.230161	H	-10.083919	-7.506068	1.449673	H	-10.145453	-7.768436	1.452798
C	-10.112901	-1.571969	-0.063107	C	10.569278	-1.106739	0.151384	C	10.368135	-1.319053	0.134215
C	-10.601167	-1.851275	1.381060	C	11.112020	-1.169825	-1.298878	C	10.921530	-1.562365	-1.292881
C	-10.521127	-2.768221	-0.959931	C	11.040178	-2.374768	0.907823	C	10.781375	-2.513146	1.031692
C	-10.857018	-0.321444	-0.578270	C	11.208736	0.117638	0.840581	C	11.048623	-0.051477	0.693627
H	-10.094801	-2.736843	1.782798	H	10.680412	-2.030801	-1.822793	H	10.461692	-2.458946	-1.724999
H	-10.322562	-1.007074	2.024798	H	10.789530	-0.272931	-1.843211	H	10.639768	-0.719330	-1.936847
C	-12.121607	-2.069804	1.412973	C	12.644572	-1.278492	-1.306566	C	12.448658	-1.729467	-1.267409
H	-10.012488	-3.679266	-0.623426	H	10.606994	-3.269474	0.445503	H	10.317532	-3.435935	0.663815
H	-10.185586	-2.578694	-1.987651	H	10.666690	-2.338203	1.939271	H	10.399384	-2.349133	2.047567
C	-12.041611	-2.985703	-0.924801	C	12.572835	-2.481990	0.897119	C	12.308633	-2.678949	1.054257
H	-10.598609	0.547900	0.040504	H	10.904349	1.037650	0.324532	H	10.784384	0.817192	0.076259
H	-10.542247	-0.096807	-1.605837	H	10.852780	0.190692	1.876639	H	10.687015	0.148107	1.710928
C	-12.379155	-0.532443	-0.547790	C	12.742439	0.016389	0.835440	C	12.577138	-0.210745	0.720370
H	-12.433427	-2.271157	2.444596	H	12.995472	-1.327829	-2.344105	H	12.807174	-1.906486	-2.288321
C	-12.484685	-3.267491	0.520141	C	13.070601	-2.550604	-0.555783	C	12.817226	-2.926248	-0.375402
C	-12.830796	-0.810218	0.893946	C	13.248411	-0.048047	-0.613570	C	13.093900	-0.453905	-0.705736
H	-12.296475	-3.840839	-1.561811	H	12.872501	-3.390476	1.432726	H	12.567426	-3.533541	1.690501
C	-12.750905	-1.725256	-1.441555	C	13.176827	-1.250430	1.587962	C	12.953934	-1.402429	1.613765
H	-12.870734	0.374197	-0.919821	H	13.158279	0.900983	1.332055	H	13.022670	0.706795	1.122478
H	-13.566864	-3.446844	0.553346	H	14.163378	-2.650123	-0.574565	H	13.905386	-3.068768	-0.368094
H	-11.995064	-4.176378	0.892990	H	12.656921	-3.437177	-1.053463	H	12.373779	-3.845974	-0.778266
H	-12.591979	0.047574	1.535643	H	12.964618	0.864730	-1.152939	H	12.851188	0.403921	-1.346003
H	-13.919109	-0.947207	0.928044	H	14.344267	-0.105198	-0.627730	H	14.186766	-0.553897	-0.698559
H	-12.454709	-1.525481	-2.479334	H	12.841588	-1.202386	2.631961	H	12.610768	-1.226522	2.641395
H	-13.838173	-1.874183	-1.437996	H	14.271757	-1.323185	1.602351	H	14.044963	-1.514913	1.651389
				C	-4.460032	-0.937393	1.227003	N	-3.641495	-0.344697	1.339278
				O	-3.587666	-0.319708	0.753634	N	-4.450334	-0.983132	1.728570
				O	-5.335007	-1.524430	1.714157				

Table S4. Cartesian coordinates of NAN-3, NAN-3/CO_2 and NAN-3/N_2 complexes

NAN-3				**NAN-3/CO_2 complex**				**NAN-3/N_2 complex**			
C	-3.490191	-1.361904	-0.977269	C	-3.339790	-1.629175	-0.719174	C	-3.393938	-1.612005	-0.679552
C	-3.090220	-0.471508	0.023257	C	-2.923811	-0.831453	0.350931	C	-2.982556	-0.759373	0.348394
C	-1.749155	-0.146786	0.179755	C	-1.588731	-0.470061	0.477904	C	-1.647655	-0.395587	0.465216
C	-0.760652	-0.689055	-0.652481	C	-0.626411	-0.875921	-0.457160	C	-0.681717	-0.851319	-0.441616
C	-1.174532	-1.586764	-1.641794	C	-1.054372	-1.692025	-1.508441	C	-1.105882	-1.721285	-1.451585
C	-2.515239	-1.925635	-1.796799	C	-2.387216	-2.073364	-1.632752	C	-2.438031	-2.107410	-1.562172
H	-3.814077	-0.053917	0.718080	H	-3.635916	-0.508092	1.105125	H	-3.696705	-0.397016	1.082985
H	-2.820090	-2.637285	-2.556900	H	-2.701884	-2.718918	-2.446254	H	-2.750455	-2.792919	-2.343146
C	-4.917645	-1.779236	-1.193629	C	-4.767370	-2.056829	-0.911882	C	-4.821252	-2.040193	-0.865745

O	-5.195443	-2.882840	-1.640041	O	-5.046167	-3.165167	-1.345775	O	-5.105448	-3.159349	-1.265205
N	-5.847238	-0.828522	-0.864629	N	-5.688541	-1.100815	-0.578145	N	-5.741266	-1.069925	-0.566046
H	-5.485334	0.083826	-0.632985	H	-5.322372	-0.176315	-0.399308	H	-5.368839	-0.145304	-0.408251
C	-7.254402	-0.916052	-0.903782	C	-7.095616	-1.180647	-0.639814	C	-7.148645	-1.144534	-0.626136
C	-7.978836	0.235384	-0.591253	C	-7.815464	0.004442	-0.481576	C	-7.865429	0.043512	-0.478707
C	-7.951488	-2.085631	-1.221499	C	-7.794658	-2.376543	-0.827459	C	-7.852148	-2.339641	-0.802067
C	-9.369415	0.224305	-0.592021	C	-9.206178	-0.000349	-0.507894	C	-9.256149	0.043656	-0.504528
H	-7.455099	1.155844	-0.342416	H	-7.287018	0.944235	-0.339370	H	-7.335623	0.983747	-0.343610
C	-9.341554	-2.073249	-1.215228	C	-9.184170	-2.356913	-0.850965	C	-9.241562	-2.315416	-0.825020
H	-7.407732	-2.984923	-1.474280	H	-7.253561	-3.302511	-0.963356	H	-7.313904	-3.268382	-0.928805
C	-10.090012	-0.931801	-0.903405	C	-9.929246	-1.181684	-0.694174	C	-9.983093	-1.136697	-0.678882
H	-9.883944	1.144846	-0.341946	H	-9.718652	0.946292	-0.381447	H	-9.765254	0.993112	-0.386777
H	-9.851058	-2.998852	-1.467149	H	-9.695808	-3.303379	-0.999879	H	-9.756317	-3.261458	-0.964833
C	0.702422	-0.300434	-0.441357	C	0.822710	-0.419502	-0.296575	C	0.769057	-0.394485	-0.295184
C	0.864267	1.226846	-0.599047	C	0.880932	1.123565	-0.301583	C	0.839111	1.145434	-0.383335
C	1.643359	-0.986954	-1.445754	C	1.728017	-0.934724	-1.427892	C	1.680016	-0.976124	-1.389043
C	1.142654	-0.704737	0.982202	C	1.385931	-0.936969	1.044052	C	1.317785	-0.841714	1.076312
H	0.567262	1.529009	-1.611007	H	0.493070	1.506127	-1.253157	H	0.465758	1.478317	-1.359425
H	0.188765	1.740686	0.091832	H	0.228491	1.517758	0.483909	H	0.180899	1.586858	0.371466
C	2.318687	1.671292	-0.329678	C	2.320988	1.634647	-0.080731	C	2.281236	1.657886	-0.177301
H	1.339614	-0.725321	-2.465170	H	1.335321	-0.591108	-2.390957	H	1.297550	-0.682661	-2.372712
H	1.569572	-2.077991	-1.356768	H	1.727194	-2.031687	-1.450918	H	1.671581	-2.072699	-1.352914
C	3.115033	-0.572860	-1.223708	C	3.183908	-0.447213	-1.259488	C	3.138119	-0.490378	-1.234724
H	0.502580	-0.228861	1.733968	H	0.773804	-0.583917	1.882053	H	0.701384	-0.439074	1.888410
H	1.009288	-1.786271	1.096238	H	1.326216	-2.030998	1.050973	H	1.249184	-1.933239	1.142240
C	2.609610	-0.306828	1.254592	C	2.842378	-0.471507	1.260805	C	2.775848	-0.376025	1.280424
C	3.230508	0.961361	-1.342639	C	3.198016	1.095566	-1.221535	C	3.163903	1.051898	-1.279832
C	2.728603	1.217686	1.088401	C	2.858344	1.066604	1.250938	C	2.803534	1.158967	1.187904
C	3.516604	-0.979111	0.203144	C	3.710475	-0.969497	0.086667	C	3.649727	-0.942832	0.142264
H	4.277483	1.248327	-1.184050	H	4.234431	1.435529	-1.102988	H	4.201919	1.390010	-1.170333
H	2.959813	1.270536	-2.358130	H	2.835498	1.487148	-2.178228	H	2.812850	1.394645	-2.259362
H	2.095712	1.715282	1.832010	H	2.252374	1.441757	2.083471	H	2.193797	1.583128	1.993803
H	3.760158	1.542681	1.271863	H	3.879368	1.438876	1.400421	H	3.826056	1.531851	1.325194
H	3.450534	-2.068042	0.306228	H	3.718907	-2.065240	0.076098	H	3.649696	-2.037580	0.191361
H	4.557224	-0.695785	0.404278	H	4.743501	-0.637964	0.249524	H	4.684075	-0.610688	0.295568
C	-11.615717	-0.987156	-0.915425	C	-11.454821	-1.231203	-0.732485	C	-11.508868	-1.181346	-0.716142
C	-12.262750	0.362469	-0.537469	C	-12.101101	0.158656	-0.549636	C	-12.150230	0.212206	-0.544510
C	-12.116263	-2.050561	0.094805	C	-11.983979	-2.150920	0.397029	C	-12.040945	-2.090015	0.420860
C	-12.121756	-1.374932	-2.327985	C	-11.932987	-1.799587	-2.092727	C	-11.988973	-1.759117	-2.071680
H	-11.932682	0.666860	0.464514	H	-11.791489	0.590596	0.411108	H	-11.838588	0.651059	0.412473
H	-11.937968	1.141572	-1.239552	H	-11.755222	0.837752	-1.339944	H	-11.802641	0.883507	-1.340731
C	-13.796563	0.266083	-0.560424	C	-13.634637	0.065411	-0.594329	C	-13.684123	0.123975	-0.588025
H	-11.768763	-1.782844	1.100983	H	-11.656403	-1.754694	1.366838	H	-11.712120	-1.687048	1.387489
H	-11.678612	-3.027426	-0.142278	H	-11.547385	-3.151936	0.299740	H	-11.607842	-3.093330	0.331920
C	-13.648929	-2.154053	0.067854	C	-13.516352	-2.251526	0.349996	C	-13.573758	-2.185841	0.374596
H	-11.777897	-0.625043	-3.051941	H	-11.569099	-1.152392	-2.901064	H	-11.622844	-1.119988	-2.885399
H	-11.683980	-2.333034	-2.632082	H	-11.495177	-2.790826	-2.259127	H	-11.554594	-2.753281	-2.229770
C	-13.654488	-1.478889	-2.351821	C	-13.465322	-1.900844	-2.136867	C	-13.521757	-1.855148	-2.114960
H	-14.217653	1.240880	-0.287412	H	-14.055448	1.069084	-0.461517	H	-14.101396	1.130152	-0.463219
C	-14.260303	-0.797047	0.446741	C	-14.126882	-0.854208	0.533427	C	-14.179405	-0.784944	0.546983
C	-14.265821	-0.122441	-1.970503	C	-14.076075	-0.504049	-1.951092	C	-14.127521	-0.454656	-1.940228
H	-13.969707	-2.917658	0.786234	H	-13.857493	-2.912697	1.155345	H	-13.916987	-2.839370	1.185273
C	-14.109997	-2.547609	-1.344961	C	-13.949427	-2.826058	-1.008604	C	-14.008887	-2.769653	-0.979394
H	-13.979307	-1.760440	-3.360388	H	-13.769988	-2.311620	-3.106637	H	-13.827904	-2.272493	-3.081449
H	-15.355774	-0.862308	0.448050	H	-15.222541	-0.914816	0.518990	H	-15.275327	-0.841712	0.533085
H	-13.951376	-0.515173	1.461534	H	-13.837956	-0.442368	1.508922	H	-13.889001	-0.366427	1.519217
H	-13.960882	0.644537	-2.693943	H	-13.750879	0.159819	-2.762344	H	-13.800107	0.201582	-2.756792
H	-15.361351	-0.178973	-2.000800	H	-15.171075	-0.560157	-1.997756	H	-15.222757	-0.507282	-1.986504
H	-13.691094	-3.524591	-1.618567	H	-13.530933	-3.832027	-1.141825	H	-13.593873	-3.778109	-1.104546
H	-15.202695	-2.646336	-1.369940	H	-15.041956	-2.923391	-1.044769	H	-15.101802	-2.863470	-1.014659
H	-1.474268	0.536500	0.977736	H	-1.298347	0.139236	1.328724	H	-1.361021	0.258876	1.283011
H	-0.452581	-2.042880	-2.308872	H	-0.351636	-2.043317	-2.254526	H	-0.399436	-2.112782	-2.173911
C	2.416068	3.194143	-0.425206	C	2.316737	3.162243	-0.020403	C	2.287917	3.186576	-0.198809

C	1.654000	3.995087	0.436100	C	1.577725	3.817250	0.974088	C	1.542794	3.898281	0.751010
C	3.234867	3.846342	-1.352570	C	3.014782	3.960045	-0.932440	C	3.002343	3.929946	-1.143618
C	1.717469	5.381535	0.387077	C	1.548175	5.202755	1.065372	C	1.522842	5.286781	0.768697
H	0.985177	3.535601	1.157792	H	1.001118	3.241789	1.692232	H	0.953548	3.365264	1.491365
C	3.294111	5.235046	-1.415988	C	2.979461	5.348808	-0.855202	C	2.976747	5.321040	-1.140170
H	3.841439	3.277287	-2.047111	H	3.598197	3.507332	-1.725412	H	3.591049	3.431619	-1.904753
C	2.549002	6.018869	-0.538249	C	2.258917	5.986472	0.151896	C	2.249796	6.016043	-0.176488
H	1.078764	5.958275	1.050883	H	0.930542	5.663627	1.831792	H	0.899682	5.791968	1.501971
H	3.920245	5.727504	-2.152589	H	3.510863	5.955378	-1.581025	H	3.520769	5.884823	-1.890702
C	3.996363	-1.231121	-2.286002	C	4.025240	-0.931250	-2.441034	C	3.984455	-1.045525	-2.380848
C	5.047149	-2.094898	-1.968978	C	5.150964	-1.743398	-2.286578	C	5.100010	-1.859534	-2.172368
C	3.756872	-0.978386	-3.645378	C	3.671032	-0.561036	-3.747410	C	3.643332	-0.745401	-3.708492
C	5.835375	-2.671867	-2.963435	C	5.901539	-2.157254	-3.385886	C	5.852417	-2.344249	-3.240974
H	5.266820	-2.341801	-0.937025	H	5.460881	-2.076598	-1.303182	H	5.399061	-2.139278	-1.169087
C	4.529392	-1.557524	-4.640145	C	4.406126	-0.978234	-4.846221	C	4.379885	-1.233633	-4.776546
H	2.947292	-0.317838	-3.941429	H	2.800113	0.064840	-3.918166	H	2.781038	-0.120123	-3.920438
C	5.590946	-2.402812	-4.308939	C	5.542969	-1.771860	-4.676375	C	5.505570	-2.030162	-4.553775
H	6.616868	-3.367011	-2.667984	H	6.746867	-2.819304	-3.217561	H	6.688825	-3.005343	-3.029746
H	4.320368	-1.367047	-5.687519	H	4.109572	-0.698675	-5.851647	H	4.092642	-1.008927	-5.798300
C	3.017053	-0.773032	2.652324	C	3.375936	-1.050848	2.571045	C	3.293700	-0.888619	2.624344
C	2.942790	-2.133581	2.980210	C	3.407474	-2.439964	2.754090	C	3.310089	-2.266098	2.881687
C	3.482587	0.101584	3.639328	C	3.856181	-0.253837	3.615034	C	3.773460	-0.041197	3.628168
C	3.301023	-2.598980	4.238791	C	3.880424	-3.008086	3.929811	C	3.767231	-2.774738	4.090318
H	2.606976	-2.854249	2.240600	H	3.064875	-3.101173	1.963778	H	2.967566	-2.965495	2.124914
C	3.854114	-0.359110	4.898468	C	4.342314	-0.816498	4.791043	C	4.244010	-0.544542	4.836972
H	3.568607	1.162847	3.438024	H	3.863652	0.825960	3.524461	H	3.792113	1.032095	3.479592
C	3.754300	-1.711006	5.218626	C	4.346658	-2.197913	4.969115	C	4.232328	-1.914369	5.088958
H	3.260745	-3.667877	4.431118	H	3.918265	-4.091419	4.008051	H	3.793650	-3.852554	4.227413
H	4.231117	0.328038	5.648701	H	4.728830	-0.186982	5.585682	H	4.630037	0.123000	5.600300
C	2.656893	7.511905	-0.667015	C	2.257896	7.488729	0.169994	C	2.260325	7.517231	-0.237846
O	2.913924	8.039909	-1.738493	O	2.388820	8.135852	-0.858146	O	2.406931	8.108224	-1.297163
N	2.459964	8.202806	0.501069	N	2.114518	8.046359	1.414614	N	2.107428	8.140731	0.974279
H	2.388428	7.644540	1.337873	H	2.151432	7.405728	2.192648	H	2.135827	7.542106	1.785538
C	4.180306	-2.136824	6.595144	C	4.891848	-2.735303	6.261961	C	4.758949	-2.388524	6.413799
O	5.026993	-1.513216	7.217874	O	5.742451	-2.126082	6.893508	O	5.612657	-1.758777	7.020092
N	3.537444	-3.247758	7.076970	N	4.349142	-3.929490	6.660686	N	4.195311	-3.552641	6.869494
H	2.769567	-3.590756	6.520379	H	3.565027	-4.261252	6.120120	H	3.407053	-3.897004	6.342928
C	6.381333	-3.006452	-5.435236	C	6.289548	-2.196868	-5.909068	C	6.251888	-2.537966	-5.754922
O	5.872459	-3.211743	-6.527113	O	5.718628	-2.330104	-6.981270	O	5.683621	-2.729082	-6.819561
N	7.690029	-3.282561	-5.134254	N	7.632741	-2.399634	-5.724177	N	7.591517	-2.747328	-5.550706
H	8.018993	-2.945360	-4.242549	H	8.000612	-2.129027	-4.825002	H	7.960006	-2.420770	-4.670494
C	8.676412	-3.883022	-5.943116	C	8.598240	-2.836133	-6.654210	C	8.555567	-3.249042	-6.449066
C	8.417535	-4.403324	-7.215164	C	8.285852	-3.243824	-7.954991	C	8.241694	-3.742880	-7.719515
C	9.971043	-3.960600	-5.414375	C	9.929887	-2.864776	-6.221187	C	9.886846	-3.254703	-6.014272
C	9.455894	-4.993069	-7.933317	C	9.309173	-3.674520	-8.797062	C	9.263122	-4.234690	-8.529763
H	7.421537	-4.337862	-7.629373	H	7.260304	-3.215060	-8.294755	H	7.216490	-3.732445	-8.061253
C	10.995326	-4.550705	-6.143608	C	10.938375	-3.295799	-7.073400	C	10.893538	-3.747381	-6.834734
H	10.177292	-3.556559	-4.425891	H	10.177585	-2.547849	-5.210684	H	10.135721	-2.871024	-5.027285
C	10.743465	-5.072491	-7.411148	C	10.633503	-3.704912	-8.370335	C	10.587138	-4.242221	-8.101150
H	9.245790	-5.394172	-8.919929	H	9.057588	-3.988966	-9.805172	H	9.010343	-4.615980	-9.514427
H	11.992487	-4.601529	-5.717910	H	11.964779	-3.310797	-6.720674	H	11.919758	-3.743175	-6.481129
H	11.541805	-5.533692	-7.983021	H	11.419318	-4.041699	-9.038284	H	11.371529	-4.627394	-8.744327
C	2.455006	9.596295	0.715104	C	2.035023	9.408496	1.769754	C	2.039997	9.520456	1.256503
C	2.552934	10.534823	-0.317104	C	1.975238	10.445938	0.833785	C	1.997966	10.507936	0.266547
C	2.330961	10.035049	2.039387	C	2.001442	9.708087	3.137487	C	1.999422	9.891903	2.606459
C	2.522767	11.892963	-0.006720	C	1.880453	11.761911	1.281927	C	1.914028	11.846604	0.643983
H	2.657012	10.199776	-1.339285	H	2.009801	10.218815	-0.222223	H	2.037432	10.225241	-0.775931
C	2.303531	11.392502	2.332055	C	1.907844	11.025381	3.567808	C	1.916991	11.230973	2.966061
H	2.255671	9.308777	2.845505	H	2.049340	8.904700	3.869086	H	2.032949	9.127536	3.379909
C	2.399226	12.332796	1.307845	C	1.846192	12.063590	2.640108	C	1.873316	12.219604	1.984352
H	2.599775	12.614381	-0.814239	H	1.834762	12.560790	0.548330	H	1.882106	12.606310	-0.131204
H	2.207630	11.713907	3.364345	H	1.883913	11.238586	4.631811	H	1.887479	11.500079	4.017371
H	2.378742	13.393791	1.533526	H	1.773689	13.093488	2.973430	H	1.809425	13.266363	2.262495

C	3.729789	-3.919945	8.301379	C	4.664195	-4.711259	7.790978	C	4.486074	-4.276317	8.044050
C	2.860134	-4.979806	8.587808	C	3.876578	-5.847054	8.017354	C	3.671101	-5.379212	8.328531
C	4.737579	-3.587863	9.212445	C	5.714124	-4.413120	8.665425	C	5.538916	-3.954658	8.906540
C	2.993740	-5.701257	9.767133	C	4.132701	-6.676898	9.101265	C	3.902867	-6.153601	9.457996
H	2.074361	-5.241238	7.882727	H	3.058404	-6.082417	7.340518	H	2.850612	-5.632632	7.661082
C	4.858868	-4.322285	10.390440	C	5.958616	-5.256475	9.747441	C	5.758734	-4.742367	10.034771
H	5.405155	-2.765474	8.998240	H	6.318546	-3.532988	8.498081	H	6.164535	-3.099298	8.694092
C	3.997039	-5.376407	10.678333	C	5.178533	-6.386237	9.975435	C	4.951395	-5.839439	10.320506
H	2.310426	-6.519219	9.972370	H	3.511597	-7.552543	9.261215	H	3.260672	-7.004466	9.662594
H	5.644052	-4.057531	11.091772	H	6.775710	-5.017455	10.421004	H	6.578370	-4.485600	10.698644
H	4.103428	-5.938138	11.600389	H	5.380651	-7.032622	10.823004	H	5.134786	-6.442531	11.203581
				C	-3.213137	1.705927	-1.737594	N	-3.202060	1.406338	-2.197571
				O	-4.236262	1.750564	-1.176920	N	-2.210108	1.360593	-2.674200
				O	-2.197838	1.680771	-2.302217				

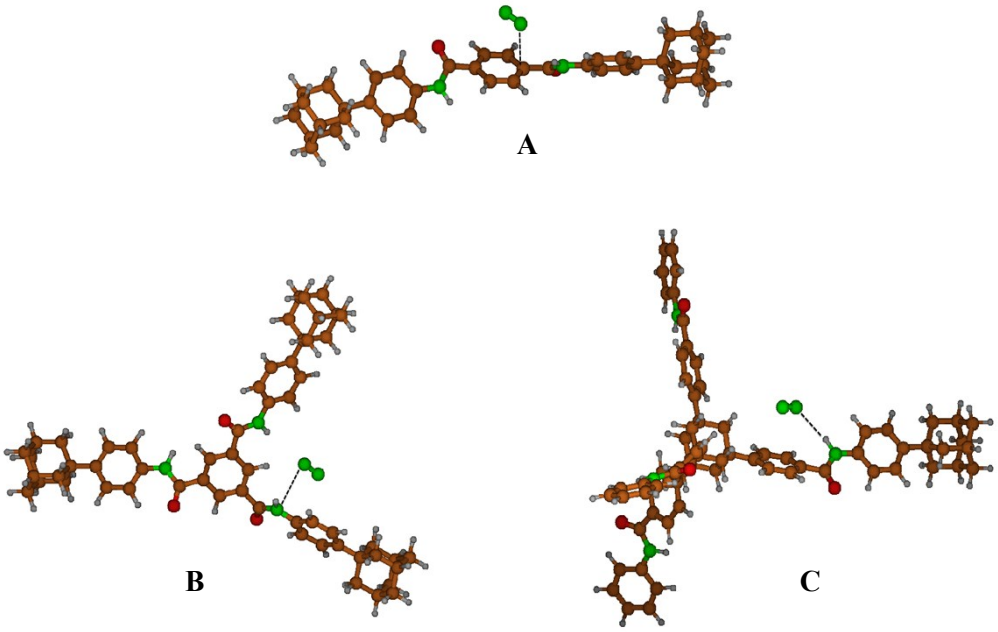


Fig. S4 Molecular models for (A) NAN-1/N_2, (B) NAN-2/N_2 and (C) NAN-3/N_2 complexes.

Calculation Methods

Isosteric heat of Adsorption (Q_{st})

Isosteric heats of adsorption for NANs were calculated from the adsorption isotherms measured at different temperatures using Clausius-Clapeyron equation:

$$\Delta_{ad}H^{\circ} = R\left[\partial lnP \Big/ \partial\left(\frac{1}{T}\right)\right]_{\theta}$$

Where, *R* is universal gas constant, θ is fraction of the adsorbed sites at a pressure *P* and temperature *T*.

CO_2/N_2 selectivity using IAST Modeling

Ideal Adsorbed Solution Theory (IAST) was used to determine CO_2/N_2 selectivity. The calculations for IAST were carried out using OriginPro 2015 version 9.2.214 program. The experimental adsorption isotherms of NANs were fitted with either a single-site Lagmuir model or a dual-site Langmuir model. These models were fitted purely on the basis of giving the best fit with adjusted r^2 values exceeding 0.98 and 0.99.

The expression for single-site Lagmuir model is given as:

$$q = \frac{q_{sat}\, bp}{1 + bp}$$

Where,

q = Adsorbed amount; q_{sat} =Saturation capacity; b = Affinity coefficient in the pure component Langmuir adsorption isotherm; p = Pressure of the bulk gas at equilibrium with the adsorbed phase

The expression for dual-site Langmuir model is as follows:

$$q = q_1 + q_2 = \frac{q_{sat,1}\, b_1 p}{1 + b_1 p} + \frac{q_{sat,2}\, b_2 p}{1 + b_2 p}$$

Where,

q = Adsorbed amount; $q_{sat,1}$ & $q_{sat,2}$ =Saturation capacities of sites 1 and 2; b_1 & b_2 = Affinity coefficients of sites 1 and 2; p = Pressure of the bulk gas at equilibrium with the adsorbed phase

IAST selectivities for the CO_2:N_2 (0.15: 0.85) gas mixtures were calculated using the following equation:

$$\alpha = \frac{q_{CO_2} / q_{N_2}}{P_{CO_2} / P_{N_2}}$$

Where, α = Selectivity; q = Adsorbed amount of each component; P = Partial pressures of each component

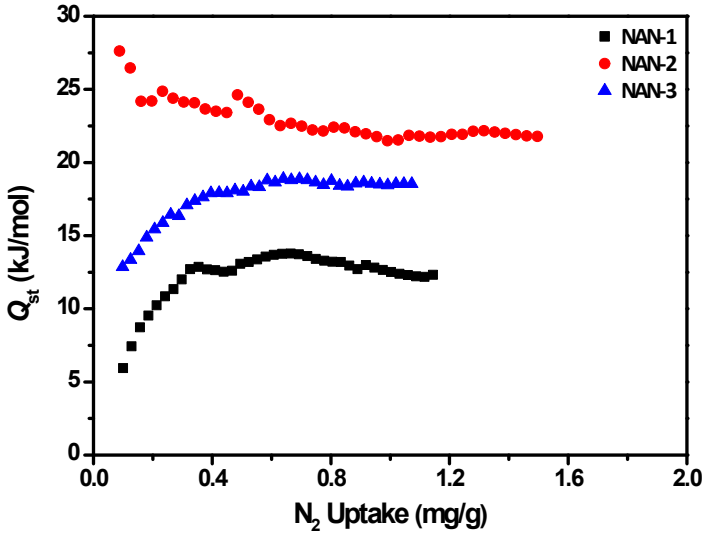


Fig. S5 Isosteric heat of N_2 adsorption for NANs.

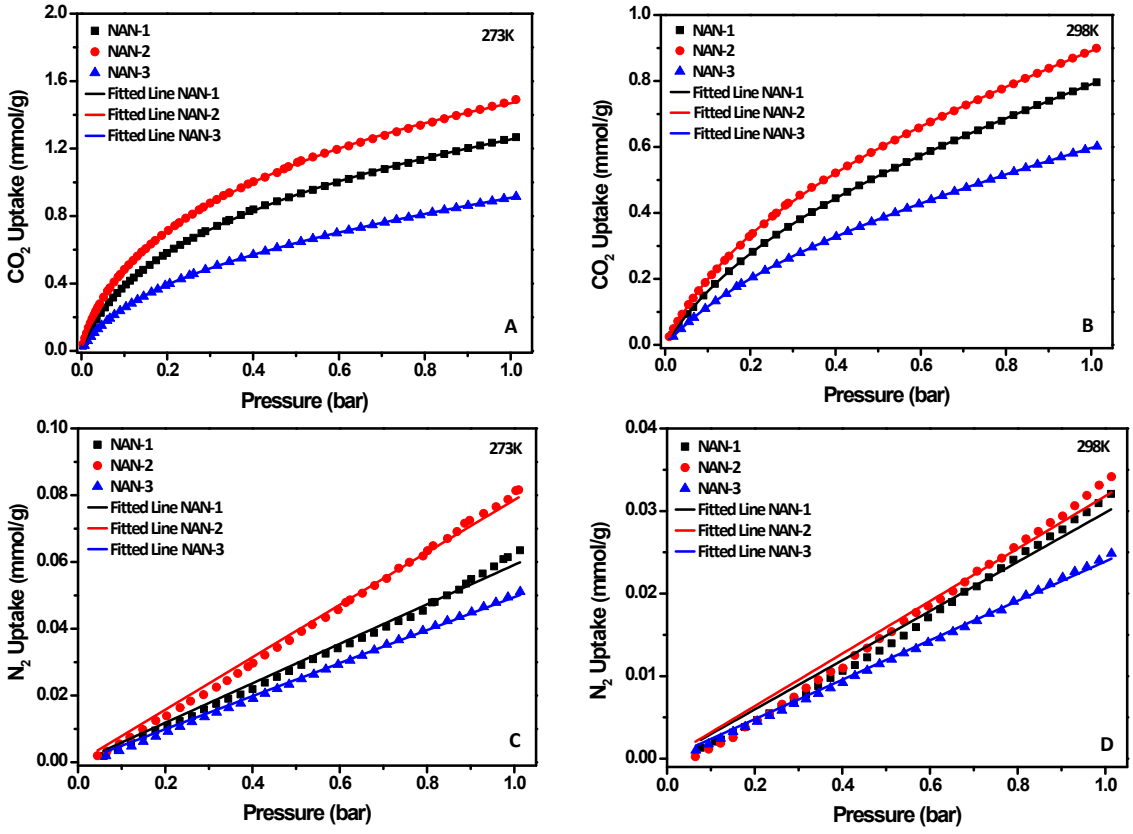


Fig. S6 CO_2 (A&B) and N_2 (C&D) isotherms fitted by Single-site Langmuir or Dual-site Langmuir models for IAST CO_2/N_2 selectivity calculations for NANs at 273K and 298K.

Table S5. IAST fitting parameters for NANs at 273K and 298K.

NANs	Temp	Fitting Parameters (CO_2)					Fitting Parameters (N_2)		
		$q_{sat,1}$	b_1	$q_{sat,2}$	b_2	R^2	q_{sat}	b	R^2
NAN-1	**273K**	0.53511	10.10729	1.94297	0.65215	0.9999	90.12619	6.56457E-4	0.99256
	298K	0.47455	3.32035	15.2226	0.02873	0.99999	51.19689	5.82407E-4	0.98346
NAN-2	**273K**	2.0031	1.00937	0.49218	15.71406	0.9999	70.90232	0.00111	0.99558
	298K	0.58176	3.66792	19.6266	0.02296	0.99996	52.38319	6.07591E-4	0.98265
NAN-3	**273K**	0.40299	8.67591	2.16499	0.33741	0.99996	31.17413	0.00159	0.99744
	298K	5.25372	0.0719	0.31975	3.24468	0.99999	15.38879	0.00156	0.99754

Single-site Langmuir or Dual-site Langmuir models were used for best fitting.

Table S6. Comparison of CO_2 adsorption data at 1 bar and CO_2/N_2 selectivity of selected porous polymers reported in literature and present work

Sorbents	CO_2 Uptake (mg/g)		CO_2/N_2 Selectivity			Reference
	T = 273K	T = 298K	Method	T = 273K	T = 298K	
NAN-1	55.78	35.02	IAST	74.0	56.4	Present Work
NAN-2	65.58	39.57	IAST	72.7	66.2	Present Work
NAN-3	40.27	26.49	IAST	57.8	50.1	Present Work
COP-94	94.1	59.1	IAST	49.8	33.9	40
Om-ph-MR	110	77.9	IAST	50	76	23
fl-CTF300	55.9	31.2	IAST	-	37	41
TBILP-1	117	78	IAST	-	62	42
APOP-2	99.9	57.2	IAST	24.3	20.2	43
CTFs	80.9	-	IAST	20.3	-	44
TPI-5	69.1	42.2	IAST	-	46.2	45
NOP-6	57.8	21.9	IAST	38.7	-	46

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